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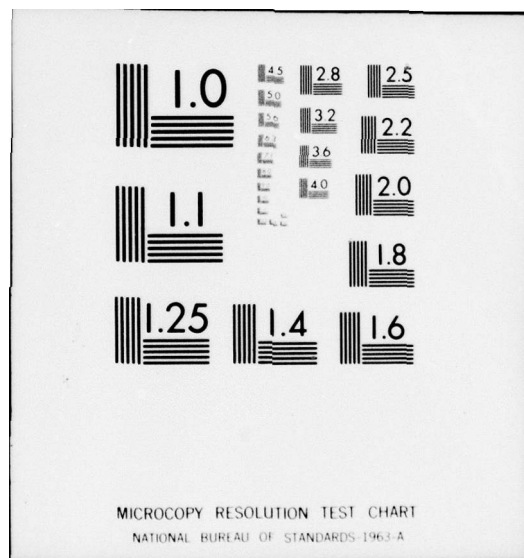
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Contract N00014-76C-0817

Task No. NR 359-623

TECHNICAL REPORT NO. 1

CHEMICAL MODIFICATION OF CARBON ELECTRODES

by

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1. REPORT NUMBER Technical Report No. 1	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER (9)	
4. TITLE (and Subtitle) (6) Chemical Modification of Carbon Electrodes.		5. TYPE OF REPORT & PERIOD COVERED Interim rept.	
7. AUTHOR(s) (10) Royce W. Murray		6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of North Carolina Chapel Hill, NC 27514		8. CONTRACT OR GRANT NUMBER(s) (15) N00014-76C-0817 new	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 359-623	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research ONR Branch Office 536 South Clark Street Chicago, Illinois 60605 (12) 16p.		12. REPORT DATE (11) Feb 1977	
15. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release, Distribution Unlimited (14) 7R-1		13. NUMBER OF PAGES 14	
		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES Prepared for publication in Journal of Electroanalytical Chemistry			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) electrochemistry, carbon electrode, porphyrin, chemically modified electrode, immobilized reagent, X-ray photoelectron spectroscopy, electrocatalysis			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Using thermally generated carboxylic acid carbon surface functionalities, tetra(aminophenyl)porphyrin is covalently bound (amide bond) to glassy carbon electrodes. The immobilized porphyrin and its <u>in situ</u> (Co(II)) metallated derivative yield clearly defined, reversible surface electrochemical waves with properties quite similar to those of the conventional solution forms. This is the first example of covalently-immobilized redox systems on carbon electrodes.			

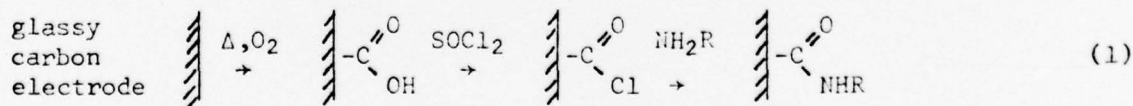
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CHEMICALLY MODIFIED ELECTRODES. VI. BINDING AND REVERSIBLE
ELECTROCHEMISTRY OF TETRA(AMINOPHENYL)PORPHYRIN ON GLASSY CARBON

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In 1975, Kariv and Miller, *et al.* [1] utilized the carboxylic acid function known [2, 3] to exist on thermally oxidized carbon to immobilize an optically active amino acid ester on graphite through formation of an amide surface bond. This "chiral electrode" was enantiomorphically selective in an electrode reaction which produced an asymmetric carbon center, although the degree of selectivity in this and a subsequent example [4] was fairly small. In these covalently modified carbon electrodes, the immobilized reagent is presumably electroinactive. We have demonstrated [5-7] that covalent immobilization of electroactive reagents can be achieved on metal oxide electrode surfaces using organosilane surface bonding.

This preliminary report applies Miller's amidization approach to carbon chemical modification to covalently bind electrochemically active reagents to glassy carbon electrode surfaces. The desired carbon surface modification chemistry is



where R is an electrochemically reactive moiety. The tetraphenylporphyrin ring system is an interesting R group because of its known well-behaved non-aqueous solution electrochemistry [8, 9], because subsequent metallation of the immobilized porphyrin could lead to a family of surface redox systems, and because adsorbed porphyrin and similar molecular systems are known to exert interesting and potentially useful electrocatalytic effects [10]. We have applied Reaction 1 to

the p and m isomers of tetra(aminophenyl)porphyrin (designated T(pNH₂)PP and T(mNH₂)PP, respectively), and present here evidence that covalent binding does occur. The surface redox reactivity of the tetraphenylporphyrins, as well as their (Co) metallated forms, is observed at potentials similar to the solution analogs.

Anson et al. [11] have described the electrochemical properties of iron(III) porphyrins which under appropriate conditions irreversibly adsorb on carbon electrodes. We also have knowledge that Kuwana and coworkers [12] have immobilized other redox systems on carbon using Miller's amidization approach [1].

Experimental

Tetra(p-aminophenyl)porphyrin, T(pNH₂)PP, was obtained by hydrolysis of tetra(p-amidophenyl)porphyrin and purified by silica gel column chromatography using 97:3 (v:v) CH₂Cl₂:CH₃OH solvent. Tetra(m-aminophenyl)porphyrin, T(mNH₂)PP, was obtained by reduction of purified tetra(m-nitrophenyl)porphyrin. Owing to solubility limitations, after thorough washing with water and CH₂Cl₂, T(mNH₂)PP was used as recovered from dimethylformamide solution. The respective p-amido and m-nitro phenylporphyrin precursors were prepared (condensation of appropriate benzaldehydes with pyrrole in propionic acid) and purified according to published procedures [13, 14]. Dimethylsulfoxide (DMSO) and toluene (distilled from Na^o) solvents were stored over molecular sieves. Thionyl chloride was twice distilled.

Glassy carbon electrodes cut from rod stock in ca. 6 mm lengths were polished on the cylinder end to a shiny finish, ending with 1 micron diamond lapping compound. Surface oxidation was by evacuation at 500°C for one hour followed by cooling in air. The electrodes were next refluxed in 5% SOCl₂ in toluene for one hour, removed and washed thoroughly with fresh solvent, and air dried for five minutes. The acid chloride electrodes were amidized by contact with a 5:1 (v:v) toluene:CH₂Cl₂ solution of the tetra(aminophenyl)porphyrin

(ca. 1 mg/50 ml) for one hour and vigorously washed with CH_2Cl_2 . The reaction medium also contained a few ml dimethylformamide in the case of $\text{T}(\text{mNH}_2)\text{PP}$.

Metallation of $\text{T}(\text{pNH}_2)\text{PP}$ and $\text{T}(\text{mNH}_2)\text{PP}$ electrodes was accomplished by a 45 minute contact with a refluxing solution of CoCl_2 in dimethylformamide followed by thorough washing with fresh solvent.

Modified electrodes were mounted for electrochemical experiments using shrinkable Teflon tubing. All electrochemical experiments were conducted in 0.1 M Et_4NClO_4 in DMSO solvent, using either conventional cyclic voltammetry or differential pulse polarography with a Princeton Applied Research Model 174 instrument under conditions as given by Anson [11]. ESCA data were obtained using a DuPont 650B Electron Spectrometer.

Results and Discussion

Cyclic voltammetry of a glassy carbon electrode reacted (see Experimental) with $\text{T}(\text{mNH}_2)\text{PP}$ is illustrated in Curve A, Figure 1. Aside from a somewhat elevated background current on the first potential scan, the pattern of two reduction and re-oxidation waves persists unchanged for many cycles. The two observed redox couples exhibit the properties expected for electrode reactions with stable, surface-immobilized reactants and products [15]; the electrochemical waves are symmetrically shaped, independent of stirring, and exhibit a linear dependence of peak current on potential scan rate over the examined 50-400 mv/sec range. The two redox couples are fairly but not precisely charge transfer reversible; ΔE_{peak} is about 30 mv at 100 mv/sec scan rate.

The meta isomer's surface wave characteristics are repeated in cyclic voltammograms of glassy carbon electrodes treated with $\text{T}(\text{pNH}_2)\text{PP}$. Curve B corresponds to a $\text{T}(\text{pNH}_2)\text{PP}$ electrode prepared from the same batch of acid chloride electrodes used to prepare the electrode of Curve A.

Anson [11] has used the proclivity of iron(III) porphyrins to adsorb under certain circumstances on carbon electrodes to observe the surface electrochemistry of these species. In order to clearly distinguish adsorption from covalent binding in the present case, a variety of control experiments were carried out. Figure 1, Curves C and D show that no observable electrochemistry ensues from treatment of acid chloride electrodes with tetraphenylporphyrin (TPP) or tetra(p-nitrophenyl)porphyrin ($T(pNO_2)PP$) under conditions identical to those used to prepare the tetra(aminophenyl)porphyrin electrodes. Curves E-H in Figure 1 show N 1s ESCA bands for a set of electrodes pretreated simultaneously through the acid chloride step and then reacted with $T(mNH_2)PP$, $T(pNH_2)PP$, TPP and $T(mNO_2)PP$, respectively. Only for electrodes treated with tetra(aminophenyl)porphyrin is there a N 1s band larger than that typical for blank glassy carbon (Curve I). These results demonstrate that the binding of the porphyrin to the acid chloride glassy carbon electrodes is associated with the presence of the amine group on the tetraphenylporphyrin. Peak diffusion currents for cyclic voltammetric reduction of a 1 mM solution of $T(pNH_2)PP$ in DMSO at unmodified glassy carbon vary linearly with the square root of potential sweep rate. Also, contact of a glassy carbon electrode for 30 minutes with a 0.01 mM $T(pNH_2)PP$ solution followed by potential sweeping in the same solution produces no porphyrin reduction waves. These observations show that the tetra(aminophenyl)porphyrin exhibits in DMSO solvent no special adsorption tendencies for the glassy carbon electrode surface. Lastly, to emphasize the surface stability of $T(pNH_2)PP$ on glassy carbon, and to rule out possible effects of material trapped in pores, a $T(mNH_2)PP$ electrode was used as a rotated disk as shown in Curve A of Figure 2. The hydrodynamic voltammogram is almost indistinguishable from the quiet solution voltammogram of Curve A, Figure 1, which was obtained with the same electrode specimen.

The preceding results provide strong evidence that association of the

tetra(aminophenyl)porphyrin with the glassy carbon electrode surface occurs through formation of surface amide bonds as depicted in Reaction 1. Our laboratory's general goal of synthetically predictive surface chemical modification appears to be realized in this case. Moreover, the potentials observed for the surface waves (-1.08 and -1.49 volt vs. S.C.E. for the two waves of T(mNH₂)PP electrode) match rather well with the known [9] values for tetraphenylporphyrin dissolved in DMSO (-1.05 and -1.47 volt). The two reduction steps for the solution TPP species [8, 9] form the porphyrin anion radical and dianion, and we presume from the good correspondence of redox potentials that the T(pNH₂)PP and T(mNH₂)PP electrode surface waves lead to these same reduction products.

While formation of four surface amide bonds per tetra(aminophenyl)porphyrin is stoichiometrically possible, this is unlikely on stereochemical grounds. The amine group's phenyl ring position would have to be optimal for proper bond directionality, and the amine sites would have to be in good register with acid chloride sites on the underlying glassy carbon electrode surface. Formation of at most two amide bonds per porphyrin might be reasonably speculated. From models, the meta (and ortho) tetra(aminophenyl)porphyrins would be more sterically suited for multiple coupling than T(pNH₂)PP. Multiple amide coupling would lead to more stable chemically modified surfaces, and also should play an important role in charge transfer rate properties of the immobilized redox system.

Our present data contain no clear evidence for the average number of surface amide bonds formed, or for any substantive differences between T(pNH₂)PP and T(mNH₂)PP electrodes. Both stability and ΔE_{peak} properties of T(mNH₂)PP and T(pNH₂)PP electrodes so far appear to be quite similar. The Curve A-B comparison of Figure 1 suggests that a higher coverage was achieved in this instance for the T(mNH₂)PP isomer. However, several T(pNH₂)PP electrodes have been prepared

with coverages equivalent to that of Curve A. The tetra(aminophenyl)porphyrin coverages are in fact not precisely reproducible; integration of the surface current peaks yields a range of $\Gamma = 3-11 \times 10^{-10}$ mole/cm² (using electrode geometrical area). The level of observed background current parallels the apparent porphyrin coverage, and comparison of Curves A in Figures 1 and 2 shows that the background current is predominantly surface-controlled. These, and other data, and coverage expectations based on molecular models, suggest to us that surface roughness factors ranging from 2-10 may exist on these chemically modified electrodes. It is most likely that such roughness is induced during the electrode thermal oxidation step. (We should note that apparent coverages in the above range are presently quite consistently obtained in current experiments, but that too-casual attention to experimental details in the overall experimental preparation process can yield apparent zero coverage). Evaluation and control of glassy carbon electrode roughening and the number of amide surface bonds per tetra(aminophenyl)porphyrin await further experimentation.

The tetra(aminophenyl)porphyrin electrodes have promise of considerable redox and electrocatalytic versatility if they can be metallated in situ without loss of the immobilized porphyrin moiety. Curves B and C of Figure 2 illustrate one successful example of this, in which Co(II) has been inserted in the porphyrin ring to definitively alter the observed surface wave redox properties from those of the immobilized free base porphyrin to those expected for the Co(II) \rightarrow Co(I) redox process for Co(II)metalloporphyrins in non-aqueous medium [9, 16, 17]. The surface wave redox potential for the Co(II) metallated electrode, -0.83 volt vs. S.C.E., is the same for T(mNH₂)PP and T(pNH₂)PP electrodes, and is in excellent agreement with that reported [9] (-0.82 and -1.87 volt) for the solution form of Co(II)TPP. The ESCA comparison of N 1s and Co 2p bands in Figure 2 is confirmatory evidence for metallation of the surface porphyrin.

Also, in one instance, the reaction conditions led to incomplete metallation; this electrode exhibited surface waves at potentials for both free and metallated porphyrin. It is encouraging to note that the tetra(aminophenyl)porphyrin electrodes survive the reaction conditions for Co(II) metallation. Experiments aimed at generating a family of immobilized metalloporphyrins are in progress.

Our electrochemical experiments in this and other [5-7] studies of chemically modified electrodes have mainly relied on the well characterized cyclic voltammetric experiment. Anson [11] has recently applied differential pulse polarography to surface waves of adsorbed species with higher sensitivity than for cyclic voltammetry. We have also observed enhanced sensitivity for the porphyrin chemically modified carbon electrodes using this method, see Figure 3. The surface waves for free base porphyrin and Co(II)-metallated porphyrin appear at the expected potentials, and again are quite stable under repeated observation. The pulse experiment detects what is apparently the reported second wave [9] for the Co(II) metalloporphyrin reduction. Also, with both $T(pNH_2)PP$ and $T(mNH_2)PP$ electrodes an additional set of electrochemical waves appears, these are not easily perceived in the cyclic voltammograms. The nature of these waves is not clear, but they vanish upon metallation of the porphyrin surface (Curve A).

Preparation of $T(NH_2)PP$ electrodes opens an array of experiments directed at both understanding and application of redox-active chemically modified electrode surfaces. These include preparation of other immobilized metallated tetraphenylporphyrins, probing of the correspondence between electrochemistry of immobilized and dissolved species, and of the effects of the metal axial ligand. Utilization of the surface-immobilized porphyrin or metalloporphyrin as a simple electron transfer mediator, or as a reactive binding site for generation of new reduction or oxidation pathways for a solution species, are electrocatalytic applications which should prove interesting.

Acknowledgement: Helpful discussions with Prof. D. G. Davis and C. E. Elliott are acknowledged as is the support of a N.S.F. Postdoctoral Fellowship (D.C.I.). This research was supported in part by the Office of Naval Research.

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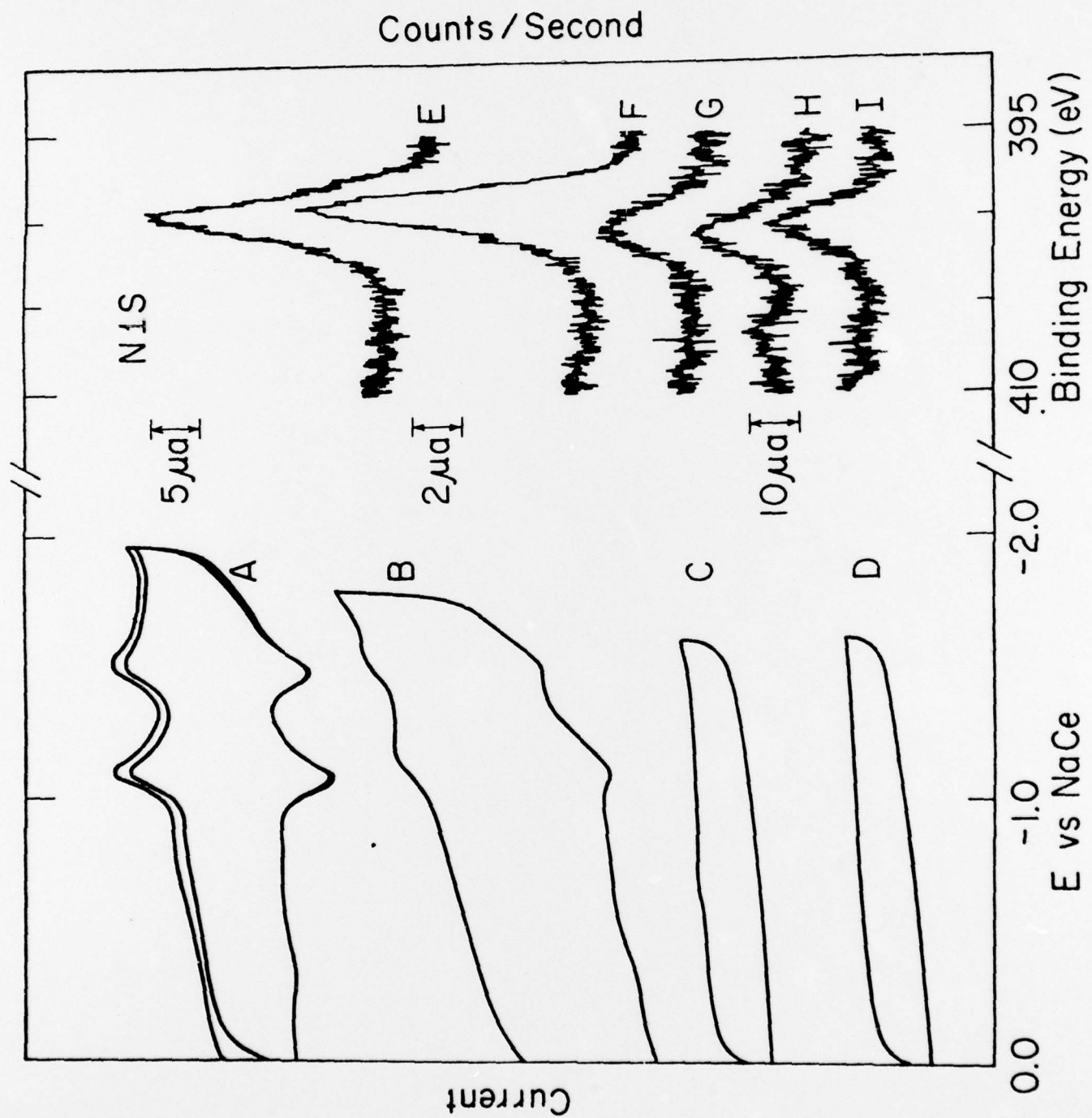
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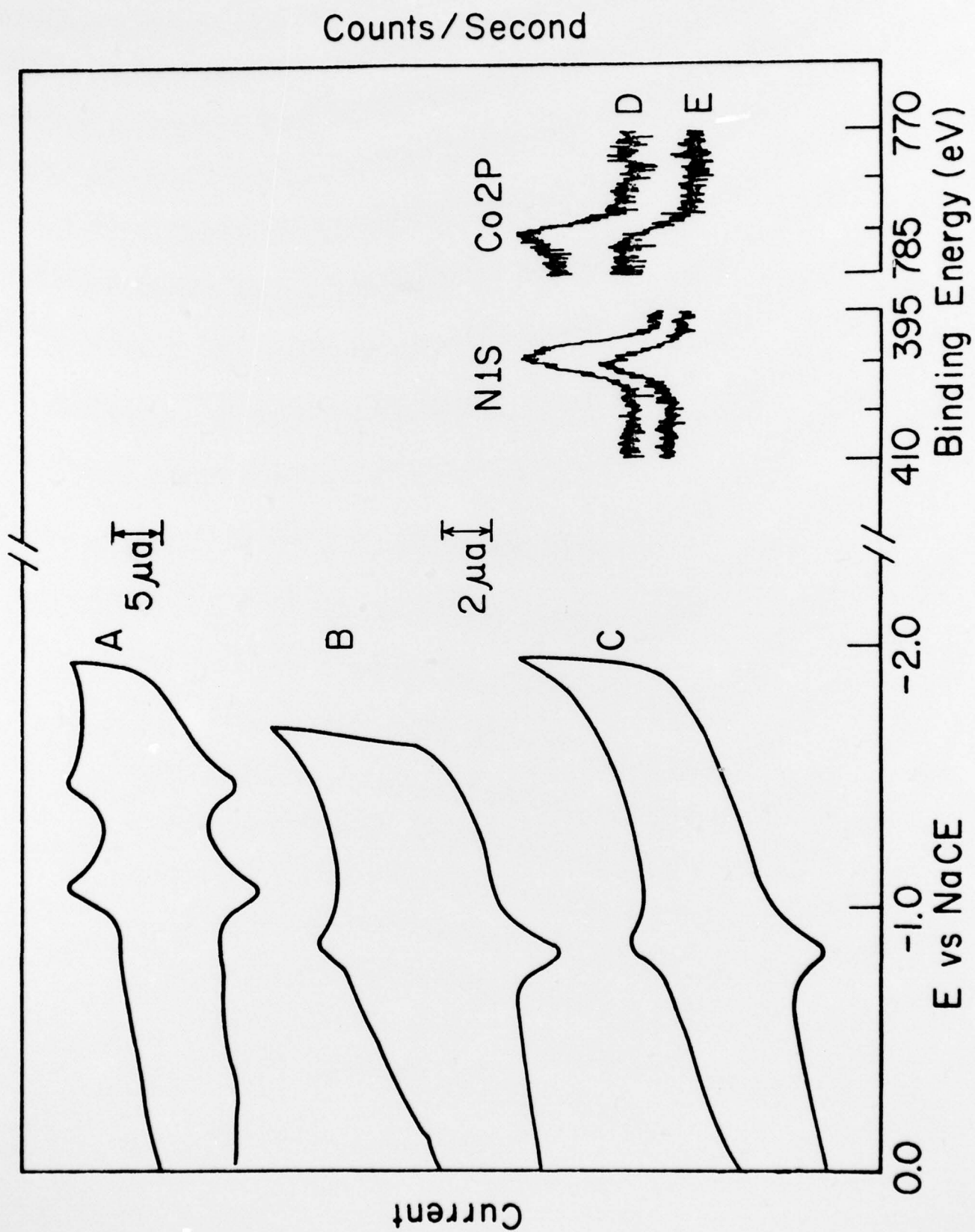
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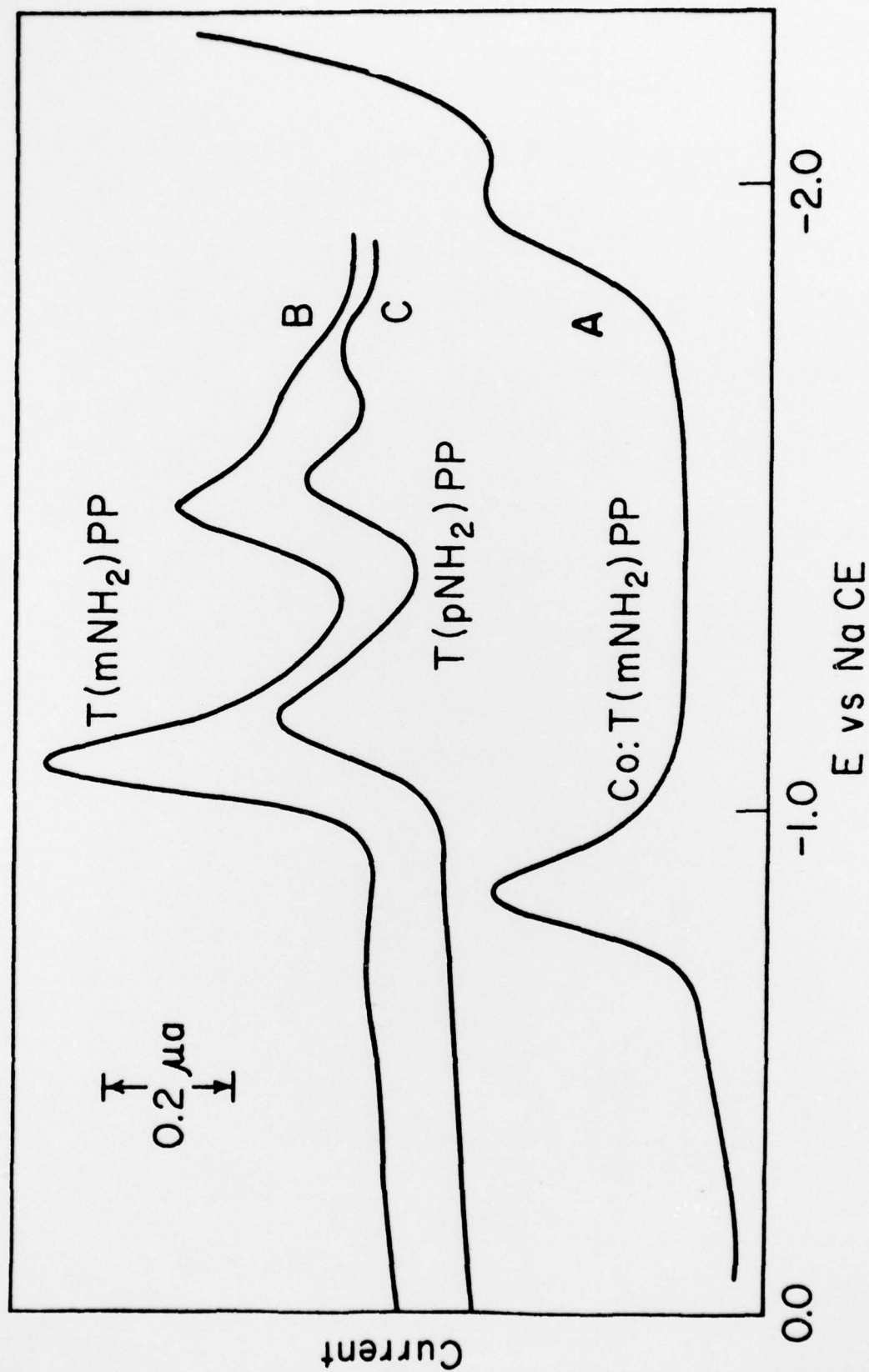
Figure 1. Cyclic voltammetry (100 mv/sec in 0.1 M $\text{Et}_4\text{NClO}_4/\text{DMSO}$) and ESCA for chemically modified glassy carbon and controls. Curve I: polished, blank glassy carbon; Curves D, H: acid chloride form of glassy carbon "reacted" with tetra(m-Nitrophenyl)porphyrin; Curves C, G: acid chloride form of glassy carbon "reacted" with tetraphenylporphyrin; Curves B, F: $\text{T(pNH}_2\text{)PP}$ electrode; Curves A, E: $\text{T(mNH}_2\text{)PP}$ electrode.

Figure 2. Assorted experiments on chemically modified glassy carbon. Curve A: A $\text{T(mNH}_2\text{)PP}$ electrode used as a rotated disk electrode, voltammogram obtained at 400 r.p.m. and 100 mv/sec; Curve B: quiet solution cyclic voltammetry at 100 mv/sec of Co-metallated $\text{T(mNH}_2\text{)PP}$ electrode; Curve C: cyclic voltammetry of Co-metallated $\text{T(pNH}_2\text{)PP}$ electrode; Curve D: ESCA of an electrode of Curve B, before electrochemical use; Curve E: blank glassy carbon "reacted" with CoCl_2 in DMF.

Figure 3. Differential pulse polarograms obtained with Princeton Applied Research Model 174 instrument with settings: pulse amplitude 10 mV; d.c. scan rate 5 mV/sec; pulse repetition rate 2/sec.







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